IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
REQUEST FOR FILING NATIONAL PHASE OF
PCT APPLICATION UNDER 35 U.S.C. 371 AND 37 CFR 1.494 OR 1.495

To: Hon. Commissioner of Patents
Washington, D.C. 20231

**

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US)

Atty Dkt: 46 /165
M# /Client Ref.

From: Manelli Dension & Selter:

Date: February 28, 2002

This is a **REQUEST** for **FILING** a PCT/USA National Phase Application based on:

1. International Application	2. International Filing Date	3. Earliest Priority Date Claimed
PCT/JP00/05993	04 September 2000	06 September 1999
⇧ country code	Day MONTH Year	Day MONTH Year (use item 2 if no earlier priority)

4. Measured from the earliest priority date in item 3, this PCT/USA National Phase Application Request is being filed within:

(a) ☐ 20 months from above item 3 date (b) ☒ 30 months from above item 3 date,

(c) Therefore, the due date (unextendable) is 06 March 2002

5. Title of Invention: ORGANIC SOLVENT-BASED DISPERSION OF CONDUCTIVE POWDERS AND CONDUCTIVE PAINT

6. Inventor(s) Kaoru ISOBE, Masanori TOMONARI and Tsutomu KIKUCHI

Applicant herewith submits the following under 35 U.S.C. 371 to effect filing:

7. ☒ Please immediately start national examination procedures (35 U.S.C. 371 (f)).

8. ☐ **A copy of the International Application** as filed (35 U.S.C. 371(c)(2)) is transmitted herewith (file if in English but, if in foreign language, file only if not transmitted to PTO by the International Bureau) including:

a. ☐ Request;
b. ☐ Abstract;
c. pgs. Spec. and Claims;
d. sheet(s) Drawing which are ☐ informal ☐ formal of size ☐ A4 ☐ 11"

9. ☒ **A copy of the International Application has been transmitted by the International Bureau.**

10. **A translation of the International Application** into English (35 U.S.C. 371(c)(2))
a. ☒ is transmitted herewith including: (1) ☐ Request; (2) ☒ Abstract;
(3) 20 pgs. Spec. and Claims;
(4) 0 sheet(s) Drawing which are:
☐ informal ☐ formal of size ☐ A4 ☐ 11"
b. ☐ is not required, as the application was filed in English.
c. ☐ is not herewith, but will be filed when required by the forthcoming PTO Missing Requirements Notice per Rule 494(c) if box 4(a) is X'd or Rule 495(c) if box 4(b) is X'd.
d. ☐ Translation verification attached (not required now).

RE: USA National Filing Of PCT /JP00/05993

11. ☒ **PLEASE AMEND** the specification before its first line by inserting as a separate paragraph:
a. ☒ --This application is the national phase of international application PCT/JP00/05993 filed 04 September 2000 which designated the U.S.--
b. ☐ --This application also claims the benefit of U.S. Provisional Application No. 60/_____, filed _____.--

12. ☐ Amendments to the claims of the International Application **under PCT Article 19 (35 U.S.C. 371(c)(3)), i.e., before 18th month from first priority date above in item 3, are transmitted herewith (file only if in English) including:**

13. ☒ PCT Article 19 claim amendments (if any) have been transmitted by the International Bureau

14. ☐ Translation of the amendments to the claims **under PCT Article 19 (35 U.S.C. 371(c)(3)), i.e., of claim amendments** made before 18th month, **is attached (required by 20th month from the date in item 3 if box 4(a) above is X'd, or 30th month if box 4(b) is X'd, or else amendments will be considered canceled).**

15. **A declaration of the inventor** (35 U.S.C. 371(c)(4))
a. ☒ is submitted herewith ☒ Original ☐ Facsimile/Copy
b. ☐ is not herewith, but will be filed when required by the forthcoming PTO Missing Requirements Notice per Rule 494(c) if box 4(a) is X'd or Rule 495(c) if box 4(b) is X'd.

16. **An International Search Report (ISR):**
a. Was prepared by ☐ European Patent Office ☒ Japanese Patent Office ☐ Other
b. ☒ has been transmitted by the international Bureau to PTO.
c. ☒ copy herewith (4 pg(s).) ☐ plus Annex of family members (___ pg(s).).

17. **International Preliminary Examination Report** (IPER):
a. ☒ has been transmitted (if this letter is filed after 28 months from date in item 3) in English by the International Bureau with Annexes (if any) in original language.
b. ☐ copy herewith in English.
c.1 ☐ IPER Annex(es) in original language ("Annexes" are amendments made to claims/spec/drawings during Examination) including attached amended:
c.2 ☐ Specification/claim pages #_____ claims # Dwg Sheets #_____
d. ☒ Translation of Annex(es) to IPER **(required by 30th month due date, or else annexed amendments will be considered canceled).**

18. **Information Disclosure Statement** including:
a. ☒ Attached Form PTO-1449 listing documents
b. ☒ Attached copies of documents listed on Form PTO-1449
c. ☒ A concise explanation of relevance of ISR references is given in the ISR.

19. ☒ **Assignment** document and Cover Sheet for recording are attached. Please mail the recorded assignment document back to the person whose signature, name and address appear at the end of this letter.

20. ☐ Copy of Power to IA agent.

21. ☐ **Drawings** (complete only if 8d or 10a(4) not completed): ___ sheet(s) per set: ☐ 1 set informal; ☐ Formal of size ☐ A4 ☐ 11"

22. Small Entity Status → ☒ is **Not** claimed ☐ is claimed (**pre**-filing confirmation required)
22(a) _____ (No.) Small Entity Statement(s) enclosed (since 9/8/00 Small Entity Statements(s) not essential to make claim)

23. **Priority** is hereby claimed under 35 U.S.C. 119/365 based on the priority claim and the certified copy, both filed in the International Application during the international stage based on the filing in (country) JAPAN of:

	Application No.	Filing Date		Application No.	Filing Date
(1)	JP 11-251356	06 September 1999	(2)		
(3)			(4)		
(5)			(6)		

a. ☒ See Form PCT/IB/304 sent to US/DO with copy of priority documents. If copy has not been received, please proceed promptly to obtain same from the IB.
b. ☒ Copy of Form PCT/IB/304 attached.

RE: USA National Filing of PCT/JP00/05993

24. Attached: 1. Form PCT/IB/308
2. Cover page of published international application WO 01/18137 (contains English Abstract)

25. **Preliminary Amendment:** ATTACHED 1. First Preliminary Amendment (enter prior to fee calculation)
2. Second Preliminary Amendment

25.5 Per Item 17.c2, **cancel original** pages #_____, claims #_____, Drawing Sheets #_____

26. **Calculation of the U.S. National Fee (35 U.S.C. 371 (c)(1)) and other fees is as follows:**
Based on amended claim(s) per above item(s) ☐ 12, ☐ 14, ☐ 17, ☒ 25, ☐ 25.5 (hilite)

Total Effective Claims	11	minus 20 =	x $18/$9 =	$0	966/967
Independent Claims	1	minus 3 =	x $84/$42 =	$0	964/965
If any proper (ignore improper) Multiple Dependent claim is present,			add$280/$140	+0	968/969

BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(4)): →→ **BASIC FEE REQUIRED, NOW** →→→→

A. If country code letters in item 1 are **not** "US","BR","BB","TT","MX","IL" "NZ", "IN" or "ZA"

See item 16 re:

1.	Search Report was not prepared by EPO or JPO - - - - - - - - -	add$1040/$520	960/961
2.	Search Report was prepared by EPO or JPO - - - - - - - - - - -	add$890/$445 +890.00	970/971

SKIP B, C, D AND E UNLESS country code letters in item 1 are "US","BR","BB","TT","MX","IL", "NZ", "IN" or "ZA"

→ (X)	☐ B.	If USPTO did not issue both International Search Report (ISR) and (if box 4(b) above is X'd) the International Examination Report (IPER), - - - - - - - - - - - - - - - - - -	add$1040/$520	+0 960/961
(only) (one) → (of)	☐ C.	If USPTO issued ISR but not IPER (or box 4(a) above is X'd), -	add$740/$370	+0 958/959
(these) (4) → (boxes)	☐ D.	If USPTO issued IPER but IPER Sec. V boxes not all 3 YES, -	add$710/$355	+0 956/957
→	☐ E.	If international preliminary examination fee was paid to USPTO and Rules 492(a)(4) and 496(b) satisfied (IPER Sec. V all 3 boxes YES for all claims), - - - - - - - - - - - - -	add $100/$50	962/963 +0

27. **SUBTOTAL =** $890.00

28. If Assignment box 19 above is X'd, add Assignment Recording fee of ----$40 +$40.00 (581)

29. Attached is a check to cover the - **TOTAL FEES** $930.00

**

Our Deposit Account No. 50-0687
Our Order No. 46 (C#) | 165 (M#)

CHARGE STATEMENT The Commissioner is hereby authorized to charge any fee specifically authorized hereafter, or any missing or insufficient fee(s) filed, or asserted to be filed, or which should have been filed herewith or concerning any paper filed hereafter, and which may be required under Rules 16-18 and 492 (missing or insufficient fee only) now or hereafter relative to this application and the resulting Official document under Rule 20, or credit any overpayment, to our Account/Order Nos. shown above for which purpose a duplicate copy of this sheet is attached.
This CHARGE STATEMENT does not authorize charge of the issue fee until/unless an issue fee transmittal form is filed

Manelli Denison & Selter
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By Atty: Paul E. White, Jr. **Reg. No.** 32,011

Sig: Paul E. White, Jr. **Fax:** 202-887-0336

Atty/Sec: / **Tel:** 202-261-1050

NOTE: File in duplicate with 2 postcard receipts (PAT-103) & attachments.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re PATENT APPLICATION of
ISOBE et al.

Group Art Unit: Not Assigned

Appln. No.: Not Assigned

Examiner: Not Assigned

Filed: February 28, 2002

International Appln. No. PCT/JP00/05993

Title: ORGANIC SOLVENT-BASED DISPERSION OF CONDUCTIVE POWDERS AND CONDUCTIVE PAINT

* * * * *

February 28, 2002

FIRST PRELIMINARY AMENDMENT: TO BE ENTERED PRIOR TO CALCULATION OF FILING FEE

Hon. Commissioner of Patents
and Trademarks
Washington, D.C. 20231

Sir:

Please enter the following Preliminary Amendment of the subject new application prior to calculation of the fee for filing the application.

IN THE CLAIMS:

Please amend claim 11 as follows (see the attached Appendix for the changes made to effect the below claim):

Claim 11. (Amended) Conductive paint obtainable by blending the organic solvent-based medium according to claim 1, and resin.

REMARKS

This Preliminary Amendment revises the multiple dependent claims to be single dependent claims and thus reduce the filing fee for the subject application. No new matter has been added.

Entry of this amendment and favorable consideration of this application are respectfully requested.

Respectfully submitted,

MANELLI DENISON & SELTER, PLLC

By _____

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APPENDIX SHOWING REVISIONS OF CLAIMS

Proposed Amendments To Claim 11 Showing Deletions And Insertions.

Claim 11. (Amended) Conductive paint obtainable by blending the organic solvent-based medium according to [any one of claims 1 through 7] claim 1, and resin.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re PATENT APPLICATION of
ISOBE et al.

Group Art Unit: Not Assigned

Appln. No.: Not Assigned

Examiner: Not Assigned

Filed: February 28, 2002

International Appln. No. PCT/JP00/05993

Title: ORGANIC SOLVENT-BASED DISPERSION OF CONDUCTIVE POWDERS AND CONDUCTIVE PAINT

* * * * *

February 28, 2002

SECOND PRELIMINARY AMENDMENT:

TO BE ENTERED AFTER CALCULATION OF FILING FEE

Hon. Commissioner of Patents
and Trademarks
Washington, D.C. 20231

Sir:

Please enter the following second Preliminary Amendment of the subject new application.

IN THE SPECIFICATION:

Please amend the specification as follows (see the attached Appendix for the changes made to effect the below changes):

Paragraph Starting at Page 15, line 5

The organic solvent-based dispersion (Sample J) was obtained in a manner similar to EXAMPLE 1, except that the powders were not coated with the silane coupling agent and the amount of dispersant CB-50 was increased to 8.0 g in EXAMPLE 1. The solid content of Sample J was 37.2 wt%.

Paragraph Starting at Page 15, line 12

The organic solvent-based dispersion (Sample K) was obtained in a manner similar to EXAMPLE 1, except that the powders were not coated with the silane coupling agent and 1.0 g of silane coupling agent AZ-6171 was added during grinding with a paint conditioner. The solid content of Sample K was 37.2 wt%.

Paragraph Starting at Page 15, line 27

The tin oxide particles in the organic solvent-based dispersions (Samples A through K) obtained in EXAMPLES 1 through 6 and COMPARATIVE EXAMPLES 2 and 3 were measured in terms of median size, using a size distribution measuring instrument, CAPA-700 (made by Shimadzu Seisakusho), which was used as an index of the dispersibility of the dispersions.

Paragraph Starting at Page 16, line 6

The solid contents of Samples A through K were diluted to 30 wt% with respective solvents. After 17 g of the diluted sample was mixed with 2.5 g of UV curing acrylic resin (DPHA: made by Nippon Kayaku K.K.), a polymerization initiator (DETX-S: made by Nippon Kayaku K.K.), a polymerization accelerator (EPA: made by Nippon Kayaku K.K.) and 7.7 g of a solvent (solvent used for each dispersion), the mixture was agitated to give conductive paint.

REMARKS

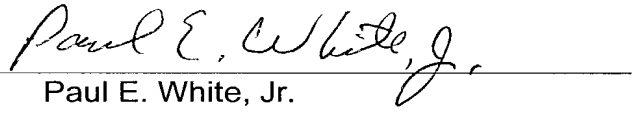
This Preliminary Amendment amends the specification to correct clerical errors. The clerical nature of the errors and the correction thereof is clear from the

context of the application. For example, the change at page 15, lines 5-6, of referring to "Sample G" to the correct "Sample J" is clearly clerical error because the name of "Sample G" is previously employed as the sample of Example 7. Similarly, the name of Sample H is previously employed as the sample of Example 8. No new matter has been added.

Entry of this amendment and favorable consideration of this application are respectfully requested.

Respectfully submitted,

MANELLI DENISON & SELTER, PLLC

By 

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APPENDIX SHOWING REVISIONS OF SPECIFICATION

Proposed Amendments To Specification Showing Deletions And Insertions.

Paragraph Starting at Page 15, line 5

The organic solvent-based dispersion (Sample [G] J) was obtained in a manner similar to EXAMPLE 1, except that the powders were not coated with the silane coupling agent and the amount of dispersant CB-50 was increased to 8.0 g in EXAMPLE 1. The solid content of Sample [G] J was 37.2 wt%.

Paragraph Starting at Page 15, line 12

The organic solvent-based dispersion (Sample [H] K) was obtained in a manner similar to EXAMPLE 1, except that the powders were not coated with the silane coupling agent and 1.0 g of silane coupling agent AZ-6171 was added during grinding with a paint conditioner. The solid content of Sample [H] K was 37.2 wt%.

Paragraph Starting at Page 15, line 27

The tin oxide particles in the organic solvent-based dispersions (Samples A through [H] K) obtained in EXAMPLES 1 through 6 and COMPARATIVE EXAMPLES 2 and 3 were measured in terms of median size, using a size distribution measuring instrument, CAPA-700 (made by Shimadzu Seisakusho), which was used as an index of the dispersibility of the dispersions.

Paragraph Starting at Page 16, line 6

The solid contents of Samples A through [H] K were diluted to 30 wt%

with respective solvents. After 17 g of the diluted sample was mixed with 2.5 g of UV curing acrylic resin (DPHA: made by Nippon Kayaku K.K.), a polymerization initiator (DETX-S: made by Nippon Kayaku K.K.), a polymerization accelerator (EPA: made by Nippon Kayaku K.K.) and 7.7 g of a solvent (solvent used for each dispersion), the mixture was agitated to give conductive paint.

DESCRIPTION

ORGANIC SOLVENT-BASED DISPERSION OF CONDUCTIVE POWDERS AND CONDUCTIVE PAINT

TECHNICAL FIELD

The present invention relates to an organic solvent-based dispersion of conductive tin oxide powders having excellent dispersibility and excellent transparency, and an organic solvent-based conductive paint using the same.

The conductive paint of the present invention is useful for static prevention of the display surface of a display device, its surface protecting material, a transparent substrate such as a film, etc., and is also useful as infrared shielding for building materials, window materials of vehicles, etc.

BACKGROUND ART

A variety of transparent substrates including display surfaces for display devices such as cathode ray tubes (CRT), liquid crystal displays (LCD), etc., window materials for clean rooms, glass or plastics used as packaging materials for IC packages, or films used for OHP or photographs, etc. are generally insulating and thus tend to be electrically charged. For this reason, dusts or trashes are apt to attach to the surfaces of these materials. In electronic

devices, static electricity causes problems of incorrect working, or the like.

Attempts to solve these problems have been made typically by kneading conductive powders into transparent substrate materials and then molding the kneaded powders, or by coating conductive powder-incorporated paints onto the surface of such substrates. Tin oxide powders are suitable as conductive powders for these applications, since they can retain excellent transparency, if uniformly dispersed in a medium, and have excellent conductive properties. For use in organic solvent-based paint, however, tin oxide powders are only sparingly dispersible in paint due to its extremely strong hydrophilicity, resulting in failure to obtain sufficient transparency.

In order to improve the dispersibility of tin oxide powders in organic solvent-based paint, there is known a method in which a dispersant such as a surfactant or the like is incorporated into paint. According to the method, it is required to incorporate large quantities of a dispersant into paint for achieving sufficient transparency, which, when coated, leads to poor adhesion to a substrate material and reduction in coating strength. Furthermore, these conductive tin oxide particles are after all coated with such a non-conductive dispersant at the surface thereof to decrease the conductivity.

DISCLOSURE OF INVENTION

The present invention has overcome the foregoing problems by providing an organic solvent-based dispersion of conductive tin oxide powders, which have excellent dispersibility even when the amount of the dispersant is minimized as possible, and when used in organic solvent-based paint, exhibit excellent transparency, conductivity and adhesion, and by providing conductive organic solvent-based paint obtainable by formulating the dispersion above.

As a result of extensive studies, the present inventors have discovered that, when conductive tin oxide powders coated with an organic metal coupling agent are dispersed in an organic solvent-based medium in the presence of a dispersant, the resulting dispersion provides a good dispersibility even in a greatly reduced amount of the dispersant to be added, and a mixture of the dispersion and resin provides excellent transparency and conductivity with excellent physical properties for coating. The present invention has thus been attained.

That is, the present invention relates to a organic solvent-based dispersion of conductive powders comprising an organic solvent-based medium as a dispersion medium, tin oxide powders coated with an organic metal coupling agent at the surface of the tin oxide particles and a dispersant. The present invention further relates to conductive paint comprising a

mixture of the dispersion and resin.

BEST MODE FOR CARRYING OUT THE INVENTION

The conductive tin oxide powders used in the present invention have a specific surface area in a range of preferably 20 to 150 m^2/g, more preferably 30 to 130 m^2/g, and most preferably 40 to 100 m^2/g. With the specific surface area much smaller than the range above, transparency and smoothness decrease when formed into a film; when the specific surface area overly exceeds the range described above, the amounts required for the dispersant and organic metal coupling agent increase, which will lead to reduction in film strength, adhesion and conductivity. The conductive tin oxide powders may take any shape without any particular restriction and is selected from spheres, needles, dendrites, plates and the like. For the purpose of improving dispersibility, oxides of silicon, tungsten, zirconium, aluminum, etc. may additionally be incorporated into the tin oxide particles to form a solid solution, or carried or coated on the surface of the tin oxide particles. Carrying or coating of these metal oxides may be effected prior to coating with the organic metal coupling agent later described, simultaneously in the co-presence of the organic metal coupling agent during manufacturing steps, or after the coating unless the purpose of the present invention is damaged. There is no particular restriction to

techniques for the carrying or coating of the metal oxides.

Preferably, the conductive tin oxide powders used in the present invention contain, in the tin oxide powders, a different type element(s) such as antimony, phosphor, fluorine, tungsten, tantalum, niobium, etc., with particular preference being antimony. The amount of antimony contained is preferably 0.5 to 20 wt%, more preferably 8 to 15 wt%, when calculated as Sb_2O_3, based on the tin oxide powders. When the amount of antimony is much smaller than the range described above, the intended effect is not obtained, and with the amount overly exceeding the range above, the powders are undesirably colored.

The conductive tin oxide powders used in the present invention may be prepared by, e.g., (1) a method which involves neutralizing a solution of a tin compound, fractionating the resulting precipitates of hydrated tin oxide and firing the hydrated tin oxide; and (2) a method which involves hydrolyzing an alcoholic solution of tin chloride in water, fractionating and firing the product; either method can be used. Where the different type element such as antimony is incorporated into the tin oxide powders according to, e.g., the method (1) above, a solution of the different type element may be added to the system during the neutralization for forming co-precipitates.

It is required for the conductive tin oxide

powders used in the present invention that the surface of the particles should be coated with the organic metal coupling agent. Merely by adding the organic metal coupling agent to the dispersion, the intended effect of improving dispersibility and sufficient transparency cannot be obtained, even when using in combination with the dispersant later described.

Examples of the organic metal coupling agent are silane coupling agents such as hexyltrimethoxy-silane, octyltrimethoxysilane, methacryloxypropyl-trimethoxysilane, etc.; titanate coupling agents such as isopropyl tris(dioctyl pyrophosphate) titanate, tetra(2,2-diallyloxymethyl-1-butyl)bis(ditridecyl)-phosphite titanate, isopropyl triisostearoyl titanate, etc.; aluminum coupling agents such as acetalkoxy aluminum diisopropylate, etc. The organic metal coupling agent may be employed alone or in combination of at least two different coupling agents.

The amount of the organic metal coupling agent coated is preferably 0.01 to 30 wt%, and more preferably 0.05 to 15 wt%, based on the conductive tin oxide powders. With the coating amount much smaller than the range above, the dispersibility of the conductive tin oxide powders in the organic solvent-based medium decreases; with the amount overly exceeding the range above, the resulting coated film encounters problems of reduced strength of the coated film, adhesion and conductivity.

The organic metal coupling agent can be coated onto the conductive tin oxide powders by, e.g., (1) a dry method which comprises adding the coupling agent or an aqueous or alcoholic solution of the coupling agent to the tin oxide powders charged in a high speed stirrer such as a Henschel mixer while agitation, uniformly stirring and then drying the mixture; (2) a wet method which comprises adding the coupling agent or an aqueous or alcoholic solution of the coupling agent to a slurry of tin oxide powders dispersed in water while agitation, thoroughly stirring, filtering, washing and then drying the mixture; any of these methods can be employed.

The dispersion of the present invention contains preferably 10 to 70 wt%, more preferably 15 to 50 wt%, of the tin oxide powders coated with the organic metal coupling agent. With the content much smaller than the range above, a problem that conductivity does not increase sufficiently occurs, when the dispersion mixing with a resin is used as conductive paint. When the organic metal coupling agent contained is too much, it becomes difficult to obtain a good dispersion from an industrial viewpoint. It is preferred that the entire surface of the tin oxide particles be coated with the organic metal coupling agent, but uncoated particles or partly coated particles may also be contained within such a range that does not damage the purpose of the invention.

In order to improve the dispersibility and stability of the conductive tin oxide powders formulated in the dispersion of the present invention, it is necessary to use dispersants. It is difficult to disperse the tin oxide powders sufficiently in the organic solvent-based medium merely by coating tin oxide with the organic metal coupling agent. Even if the amount of the coupling agent is greatly increased for the treatment, such does not eliminate the difficulty.

As the dispersants, there is usable any one of cationic dispersants such as a quaternary ammonium salts, etc.; anionic dispersants such as carboxylic acid salts, sulfonic acid salts, sulfuric acid esters, phosphoric acid esters, etc.; and nonionic dispersants of ether type, ether ester type, ester type, nitrogen-containing type, etc. There is no particular restriction so long as the dispersant is adsorbed to the conductive tin oxide powders. Among these dispersants, cationic type dispersants are preferable. Since the surfaces of the conductive tin oxide powders are usually negatively charged in a solution, the dispersant of cationic type is electrostatically adsorbed to the powders to improve the effects. The amount of the dispersant in the dispersion ranges preferably from 0.01 to 20 wt%, more preferably from 0.1 to 15 wt%, and most preferably from 0.1 to 10 wt%. With the amount of the dispersant much smaller than the

range above, the tin oxide powders tend to agglomerate in the dispersion or in the conductive paint. When the amount of the dispersant is much larger than the range above, sufficient strength of the film cannot be obtained when coated, and adhesion to a substrate is worsened. Moreover, the surface of the tin oxide powders has eventually been coated with the dispersant, which is an insulating material, so that the conductivity decreases when the dispersant is present too much.

In the present invention, the dispersant can be used alone or in combination of at least two different dispersants. When two or more dispersants are employed in combination, it is preferred to use the dispersants having different solubilities in the organic solvent-based medium as a dispersion medium. By doing so, the dispersibility of the conductive powders can be maintained more stably in preparing conductive paint.

In the dispersion of the present invention, the organic solvent-based medium as a dispersion medium has no particular restriction but may be any conventional organic solvent generally available for paint, which examples include toluene, butyl acetate, propyl alcohol, butyl alcohol, methyl ethyl ketone, xylene, etc.

The organic solvent-based dispersion of the conductive powders according to the present invention

can be prepared, e.g., by pre-mixing the conductive tin oxide powders coated with the coupling agent described above, the dispersant and the organic solvent-based medium, and dispersing the mixture through wet-grinding using a conventional grinder such as a sand mill, a ball mill, etc. The solid content in the wet grinding is preferably 10 to 80 wt%, and more preferably 30 to 60 wt%. With the solid content much higher than the range above, fluidizability decreases to make the wet grinding difficult; and with the amount overly lower than the range above, the content of the tin oxide powders in the dispersion becomes small, which is not economical. The final solid content in the dispersion can be appropriately adjusted by controlling the amount of the organic solvent-based medium, depending upon use.

The present invention further relates to conductive paint comprising the organic solvent-based dispersion described above and a resin. Any resin can be used for the conductive paint of the present invention and there is no particular limitation so long as the resin is soluble in the organic solvent-based medium described above. For use in the invention, the resin may be appropriately selected from, e.g., acrylic resin, alkyd resin, melamine resin, polyester resin, vinyl chloride-vinyl acetate resin, epoxy resin, urethane resin, phenol resin, amino resin, fluorine resin, polyvinyl alcohol resin, ethylene-vinyl acetate

copolymer, acryl-styrene copolymer, etc. The amount of the resin in the paint is preferably 5 to 90 wt%, more preferably 5 to 50 wt%.

In addition to the dispersion and resin described above, the conductive paint of the present invention may further contain additives conventionally used for paint, such as a stabilizer, a curing agent, a polymerization initiator, and the like. These additives may be used in appropriate combination depending upon purposes.

The conductive paint of the present invention can be prepared, e.g., by blending the dispersion and the resin, or by blending a solution of the resin previously prepared by dissolving the resin in a solvent and the dispersion. The conductive paint can be readily prepared by blending the dispersion and the resin or the resin solution while agitating with a blade type stirrer, a disperser, a homomixer, a dissolver, an impeller mill, etc.

The thus prepared conductive paint of the present invention is coated on a substrate such as an acrylic board, a polyvinyl board, a film, a glass plate, etc. to form a paint film having both antistatic and transparent properties. For bar coating or spray coating, a coater can be used, or ordinary coating technique such as spin coating or dip coating is available.

EXAMPLES

Hereinafter the present invention will be described below in more detail with reference to the following EXAMPLES, but is not deemed to be limited to these EXAMPLES.

EXAMPLE 1

In a juice mixer was charged 100 g of spherical antimony-containing conductive tin oxide powders (SN-100P: made by Ishihara Sangyo K.K.) having a specific surface area of 70 m^2/g. While agitating, 12.5 g of 1/4 (in a weight ratio) solution of silane coupling agent AZ-6171 (made by Nippon Unika) in ethanol was added to the powders followed by stirring. Then, the mixture was dried at 150°C for 40 minutes to coat the surface of the particles with the silane coupling agent. The amount of the silane coupling agent used for the coating was 2.5 wt% based on the antimony-containing tin oxide powders.

In a glass bottle, 40 g of the thus coated tin oxide powders, 3.2 g of cationic type dispersant CB-50 (made by Toho Chemical Co., Ltd.), 70 g of toluene and 160 g of zirconium beads were charged and ground for 90 minutes using a paint conditioner (Model #5110, made by Red Devil Co.) to give the organic solvent-based dispersion (Sample A) of the present invention. The solid content of Sample A was 38.2 wt%.

EXAMPLE 2

The organic solvent-based dispersion (Sample

B) of the invention was obtained in a manner similar to EXAMPLE 1, except that butyl acetate was used in lieu of toluene of EXAMPLE 1. The solid content of Sample B was 37.5 wt%.

EXAMPLE 3

The organic solvent-based dispersion (Sample C) of the invention was obtained in a manner similar to EXAMPLE 1, except that titanium coupling agent (KR-TTS, made by Ajinomoto) was used in lieu of the silane coupling agent of EXAMPLE 1. The solid content of Sample C was 37.2 wt%.

EXAMPLE 4

The organic solvent-based dispersion (Sample D) of the invention was obtained in a manner similar to EXAMPLE 1, except that nonionic dispersant BYK-163 (made by BYK) was used in lieu of the cationic dispersant CB-50 of EXAMPLE 1. The solid content of Sample D was 37.2 wt%.

EXAMPLE 5

The organic solvent-based dispersion (Sample E) of the invention was obtained in a manner similar to EXAMPLE 1, except that needle-like antimony-containing conductive tin oxide powders (FS-10P: made by Ishihara Sangyo K.K.) having a specific surface area of 30 m^2/g was used in lieu of the spherical antimony-containing conductive tin oxide powders of EXAMPLE 1. The solid content of Sample E was 38.0 wt%.

EXAMPLE 6

The organic solvent-based dispersion (Sample F) of the invention was obtained in a manner similar to EXAMPLE 5, except that 1.6 g of cationic dispersant CB-50 and 1.6 g of cationic dispersant OB-80E (made by Toho Chemical Co., Ltd.) were used in combination in EXAMPLE 5. The solid content of Sample F was 38.1 wt%.

EXAMPLE 7

The organic solvent-based dispersion (Sample G) of the invention was obtained in a manner similar to EXAMPLE 1, except that methyl ethyl ketone was used in place of toluene of EXAMPLE 1. The solid content of Sample G was 37.8 wt%.

EXAMPLE 8

The organic solvent-based dispersion (Sample H) of the invention was obtained in a manner similar to EXAMPLE 1, except that isopropyl alcohol was used in place of toluene of EXAMPLE 1. The solid content of Sample H was 37.3 wt%.

EXAMPLE 9

The organic solvent-based dispersion (Sample I) of the invention was obtained in a manner similar to EXAMPLE 5, except that methyl ethyl ketone was used in place of toluene of EXAMPLE 5. The solid content of Sample I was 38.0 wt%.

COMPARATIVE EXAMPLE 1

The procedures were carried out as in EXAMPLE 1 except that the powders were not coated with the

silane coupling agent. A paste-like substance was obtained but no dispersion was obtained. Thus, no further evaluation was made.

COMPARATIVE EXAMPLE 2

The organic solvent-based dispersion (Sample G) was obtained in a manner similar to EXAMPLE 1, except that the powders were not coated with the silane coupling agent and the amount of dispersant CB-50 was increased to 8.0 g in EXAMPLE 1. The solid content of Sample G was 37.2 wt%.

COMPARATIVE EXAMPLE 3

The organic solvent-based dispersion (Sample H) was obtained in a manner similar to EXAMPLE 1, except that the powders were not coated with the silane coupling agent and 1.0 g of silane coupling agent AZ-6171 was added during grinding with a paint conditioner. The solid content of Sample H was 37.2 wt%.

COMPARATIVE EXAMPLE 4

The procedures were performed as in EXAMPLE 1 except that the coating amount of the silane coupling agent was increased to 10.0 wt% and no dispersant was used. A paste-like substance was obtained but no dispersion was formed. Thus, no further evaluation was made.

TEST EXAMPLE

The tin oxide particles in the organic solvent-based dispersions (Samples A through H)

obtained in EXAMPLES 1 through 6 and COMPARATIVE EXAMPLES 2 and 3 were measured in terms of median size, using a size distribution measuring instrument, CAPA-700 (made by Shimadzu Seisakusho), which was used as an index of the dispersibility of the dispersions.

The solid contents of Samples A through H were diluted to 30 wt% with respective solvents. After 17 g of the diluted sample was mixed with 2.5 g of UV curing acrylic resin (DPHA: made by Nippon Kayaku K.K.), a polymerization initiator (DETX-S: made by Nippon Kayaku K.K.), a polymerization accelerator (EPA: made by Nippon Kayaku K.K.) and 7.7 g of a solvent (solvent used for each dispersion), the mixture was agitated to give conductive paint.

The thus obtained conductive paint was coated onto a glass plate in a dry thickness of 2.3 μm using a bar coater, subjected to natural drying and then exposed to UV rays to obtain a paint film. The surface resistivity and haze percentage (an index showing the degree a cloudy appearance of a film; the lower the haze value, the higher the transparency) of the paint film were determined using a digital ohm meter (Model R-506, made by Kawaguchi Denki Seisakusho) and a haze meter (Model NDH-300A, made by Nippon Denshoku Kogyo K.K.), respectively. Furthermore, pencil hardness was evaluated according to JIS K5400.

The results are shown in TABLE 1.

TABLE 1

	Dispersed state of dispersion	Median size of dispersion (μm)	Surface resistivity ($\Omega/\square$)	Haze percentage (%)	Pencil hardness
Ex. 1	good	0.10	3.3×10^{8}	0.64	4H
Ex. 2	good	0.09	2.6×10^{8}	0.91	4H
Ex. 3	good	0.09	4.3×10^{9}	0.52	4H
Ex. 4	good	0.09	7.8×10^{8}	0.80	4H
Ex. 5	good	0.12	4.5×10^{8}	0.95	4H
Ex. 6	good	0.09	2.3×10^{7}	1.00	4H
Ex. 7	good	0.10	8.0×10^{7}	0.61	4H
Ex. 8	good	0.09	7.5×10^{8}	0.77	4H
Ex. 9	good	0.13	5.8×10^{8}	1.07	4H
Comp. Ex. 1	poor dispersion	-	-	-	-
Comp. Ex. 2	good	0.14	6.7×10^{13}	0.78	2B
Comp. Ex. 3	good	0.18	5.9×10^{9}	2.81	2H
Comp. Ex. 4	poor dispersion	-	-	-	-

INDUSTRIAL APPLICABILITY

The present invention provides the dispersion comprising conductive tin oxide powders, the surface of which has been coated with the organic metal coupling agent, the dispersant and the organic solvent-based medium. The dispersion shows excellent dispersibility even when the amounts of the coupling agent and the dispersant are minimized as possible. Thus, the conductive paint having excellent transparency, conductivity and adhesion can be readily obtained in a simple

manner by blending the dispersion of the invention with the organic solvent-based resin or the resin solution. For this reason, the present invention can provide antistatic materials for CRT, clean room windows, films, etc. advantageously in an economical way.

CLAIMS

1. An organic solvent-based dispersion of conductive powders comprising an organic solvent-based medium as a dispersion medium, tin oxide powders coated with an organic metal coupling agent at the surface of tin oxide particles, and a dispersant.

2. The organic solvent-based dispersion according to claim 1, wherein the tin oxide powders contain antimony.

3. The organic solvent-based dispersion according to claim 1, wherein the tin oxide powders coated with the organic metal coupling agent are contained in 10 to 70 wt%.

4. The organic solvent-based dispersion according to claim 1, wherein the tin oxide powders have a specific surface area of 20 to 150 m^2/g.

5. The organic solvent-based dispersion according to claim 1, wherein at least one of a silane coupling agent, a titanate coupling agent and an aluminum coupling agent is used as the organic metal coupling agent.

6. The organic solvent-based dispersion according to claim 1, wherein the coating amount of the organic metal coupling agent is 0.01 to 30 wt%, based on the tin oxide powders.

7. The organic solvent-based dispersion according to claim 1, wherein the dispersant is contained in 0.01 to 20 wt%.

8. The organic solvent-based dispersion according to claim 1, wherein at least two dispersants are employed.

9. The organic solvent-based dispersion according to claim 8, wherein the solubilities of the dispersants in the organic solvent-based medium as a dispersion medium are different from each other.

10. The organic solvent-based dispersion according to claim 1, wherein the dispersant is a cationic dispersant.

11. Conductive paint obtainable by blending the organic solvent-based medium according to any one of claims 1 through 7, and resin.

ABSTRACT

The organic solvent-based dispersion of conductive powders of the present invention comprises an organic solvent-based medium as a dispersion medium, conductive tin oxide powders coated with an organic metal coupling agent at the surface of tin oxide particles and a dispersant, and shows excellent dispersibility and high transparency. Therefore, the dispersion is useful for antistatic purpose of transparent substrates including the display surface of display devices, their surface protecting materials, films, etc.

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(54) Title: ORGANIC SOLVENT BASED DISPERSION OF CONDUCTIVE POWDER AND CONDUCTIVE COATING MATERIAL

(54) 発明の名称: 導電性粉末有機溶剤系分散体及び導電性塗料

(57) Abstract: An organic solvent based dispersion of an electrically conductive powder which comprises an organic solvent based medium as a dispersion medium, a tin oxide powder comprising tin oxide particles having an organic metal-coupling agent coating the surface thereof, and a dispersing agent. The dispersion has excellent dispersibility and high transparency, and therefore, is suitable for use as an antistatic agent for a transparent substrate such as a displaying face of a display device, a surface protecting material therefor, a film or the like.

(57) 要約:

本発明の導電性粉末有機溶剤系分散体は、分散媒としての有機溶剤系媒体、粒子表面に有機金属カップリング剤を被覆した酸化スズ粉末及び分散剤を含有し、優れた分散性と、高度の透明性を有する。したがって、表示機器の表示面、その表面保護材料、フィルム等の透明基材の帯電防止用途に有用である。

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RULE 63 (37 C.F.R. 1.63)
DECLARATION AND POWER OF ATTORNEY FOR UTILITY OR DESIGN PATENT APPLICATION IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

[ ] Declaration Submitted with Initial Filing or [ ] Declaration Submitted after Initial Filing (surcharge 37 CFR 1.16 (e) required)

As a below named inventor, I hereby declare that my residence, post office address and citizenship are as stated below next to my name, and I believe I am the origir first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claime and for which a patent is sought on the **INVENTION ENTITLED**

"ORGANIC SOLVENT-BASED DISPERSION OF CONDUCTIVE POWDERS AND CONDUCTIVE PAINT" , the specification of which is:

[ ] attached hereto
OR
[x] was filed on (MM/DD/YYYY) September 4, 2000 As United States Application Number (Attorney Docket No. _____) or PCT International Application No. PCT/JP00/05993 and was amended on _____ (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose all information known to me to be material to patentability as defined in 37 C.F.R. 1.56 including for continuation-in-part application, material information which becomes available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application

I hereby claim foreign priority benefits under 35 U.S C. 119(a) -(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(a) of any PCT international Application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventors certificate, or any PCT international application having a filing date before that of the application on which priority is claimed.

PRIOR FOREIGN APPLICATION(S)			Priority Not Claimed	Certified Copy Attached?	
Number	Country	Foreign Filing Date (MM/DD/YYYY)		Yes	No
11-251356	Japan	September 6, 1999	[ ]	[ ]	[ ]

I hereby claim the benefit under 35 U.S.C. 119(e) of any United States provisional Application(s) listed below.

PRIOR U.S. PROVISIONAL(S)	
Application No. (series code/serial no.)	Filing Date (MM/DD/YYYY)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, unde Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

I hereby appoint the registered practitioners represented by **Customer No.: 20736** to prosecute this application and transact all business in the U S. Patent and Trademark Office in connection therewith. Direct all correspondence to **Manelli Denison & Selter PLLC at Customer No.: 20736.**

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[ ] Additional Inventors are being named on the _ supplemental additional inventor sheet(s) attached hereto. MDS Jan 2001